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Zinc(II) bis(dipyrromethenate)s crystal solvates with dimethyl sulfoxide Composition, stability and spectral-luminescent properties

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ABSTRACT

It was found that 3,3′-, 2,3′ and 2,2′-zinc(II) bis(dipyrromethenate)s ([$Zn_2\mathbf{L}_2$]) form stable supramolecular complexes of the composition [$Zn_2\mathbf{L}_2$(DMSO)$_n$] (n = 1 or 2) with dimethyl sulfoxide (DMSO). The [$Zn_2\mathbf{L}_2$(DMSO)$_n$] are stable in the solid phase and solutions. Composition, stability, and spectral-luminescent properties of the [$Zn_2\mathbf{L}_2$(DMSO)$_n$] crystal solvates were studied by means of FTIR, PXRD, ^{1}H NMR, DOSY, absorption and fluorescence analyses. Spectroscopic studies showed that the quantum yields (φ) of [$Zn_2\mathbf{L}_2$(DMSO)$_n$] are lower (to ~1.6–3.6 times) than quantum yields (φ_O) of [$Zn_2\mathbf{L}_2$] in cyclohexane. Quantum-chemical study allowed to suggest the most likely mechanism of the DMSO molecules coordination on the coordinating centers of [$Zn_2\mathbf{L}_2$]. It is demonstrated, that the high-energy coordination interactions (Zn – O) in [$Zn_2\mathbf{L}_2$(DMSO)$_n$] are the main cause of the fluorescence quenching of [$Zn_2\mathbf{L}_2$] in the presence of DMSO. Fluorescence quenching of [$Zn_2\mathbf{L}_2$] in the DMSO presence is based on the photoinduced electron transfer (PeT) mechanism. The obtained results are interesting for the development of new [$Zn_2\mathbf{L}_2$] fluorescent sensors of the DMSO molecules.

1. Introduction

Dimethyl sulfoxide (DMSO) is an important solvent with a pronounced electron-donating ability. It is less toxic than other members of this group (DMF, dimethylacetamide, N-methyl-2-pyrrolidone, HMPA) and widely used in various fields of medicine and analytical chemistry. Due to its unique solvating ability, DMSO is often used as a solvent in chemical reactions. In molecular biology DMSO is used in polymerase chain reaction to inhibit secondary structures in the DNA [1]. DMSO is used as a cryoprotectant for prevent cell death during the freezing process [2]. This solvent is used in various fields of industry and microelectronics [3].

However, the high diffusing ability of DMSO can lead to penetration through the skin of soluble in it various toxicants. The most commonly reported side effects include headaches and burning and itching on contact with the skin. Strong allergic reactions have been reported. It is a neurotoxin and in some countries, DMSO is listed as a Schedule 4 Drug [4].

It is obvious that actual problem is the development of sensors for the rapid analysis of small amounts of DMSO and other toxic compounds in various media. Therefore, fluorescent sensors are of significant interest [5–10]. From this point of view, the binuclear zinc(II) helicates ([$Zn_2\mathbf{L}_2$]) are able to become one of the most promising platform for the development of fluorescent sensors. There is a considerable interest in [$Zn_2\mathbf{L}_2$] helicates due to their high quantum yields (up to 100%) and their fluorescence sensitivity to nature and properties of the medium. Interesting regularities were found under the study of spectral-luminescent properties of these dyes in various solvents [11]. For example, fluorescence quantum yield of [$Zn_2\mathbf{L}_2$] helicates amounts up to 100% in nonpolar saturated hydrocarbons (cyclohexane, hexane, and etc.). The [$Zn_2\mathbf{L}_2$] fluorescence is significantly quenched (up to 0) in polar electron-donating solutions (acetone, DMF, DMSO, pyridine, DEA, and TEA) [12]. In this case, fluorescence quenching of [$Zn_2\mathbf{L}_2$] may be caused by means of the formation of [$Zn_2\mathbf{L}_2X_n$] supramolecular systems (X—electron-donating molecule) by additional coordination of X on coordination centers of helicates. The components mobility in supramolecular complex increase the probability of nonradiative transitions in the excited state.

To confirm this hypothesis, we obtained crystalline samples by slow crystallization from saturated solutions of [$Zn_2\mathbf{L}_2$] in N- and O-containing electron-donating solvents (X-acetone, DMF, DMSO, pyridine, DEA, and TEA) [13–17]. Thermogravimetric and

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